Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information

Efficient Temperature Sensing Platform Based on Fluorescent Block Copolymer Functionalized Graphene Oxide

Hyunseung Yang,§ Kwanyeol Paek,§ and Bumjoon J. Kim*

§ : These authors contributed equally to this work

[1]*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea*

Keywords: Graphene oxide, Stimuli-responsive polymer, Block copolymer, Temperature sensor

*E-mail:bumjoonkim@kaist.ac.kr

Materials

7-hydroxycoumarin, 1,4-dibromobutane, sodium acrylate, hydroquinone, phenyl magnesium bromide, carbon disulfide anhydrous, methyl alpha-bromophenyl acetate, 4-vinylbenzylchloride, *N*-isopropylacrylamide, hexylamine, sodium azide, potassium persulfate and phosphorus pentoxide were purchased from Sigma-Aldrich. Anhydrous K_2CO_3, $MgSO_4$, H_2SO_4 and HCl were purchased from Daejung. Azobisisobutyronitrile (AIBN) and $KMnO_4$ were purchased from Junsei. Graphite powders were purchased from Graphit Kropfmuhl.

Synthesis of 7-(4-(acryloyloxy)butoxy)coumarin(7AC)

The 7AC monomer was synthesized as reported in a previous study.[1] Anhydrous K_2CO_3 (3.48 g, 24.8 mmol) was added into a mixture of 7-hydroxycoumarin (2 g, 12.4 mmol) and 1,4-dibromobutane (4.42 mL, 37.2 mmol) in acetone (120 mL). The resulting suspension was heated to reflux for 24 h. The precipitate was filtered off, and the solvent was removed. The resulting mixture was diluted with diethyl ether and the separated organic layer was washed with DI water, dried over $MgSO_4$, and concentrated in *vacuo*. Then, the residue was purified by means of column chromatography on silica gel with mixed hexane and ethyl acetate as the eluent, resulting in 7-(4-bromobutoxy)-coumarin. Then, 7-(4-bromobutoxy)-coumarin (2.38g, 9mmol) and excess sodium acrylate (1.128 g, 12mmol) were dissolved in ethanol (150 mL). Hydroquinone (0.02 g, 1.8 mmol) was added. The solution was heated to reflux for 36 h. The precipitate was filtered off and washed with ethanol. After the solvent was removed at reduced pressure, DI water was added, and the residue was extracted with diethyl ether. Then, the residue was purified by means of column chromatography on silica gel with mixed hexane and ethyl acetate as the eluent to yield 7-(4-(acryloyloxy)butoxy)coumarin (7AC) (1.4g, 61%) as a white solid.

^{1}H NMR ($CDCl_3$): 7.62 (d, 1H), 7.34 (d, 1H), 6.80 (m, 2H), 6.41 (d, 1H), 6.24 (m, 1H), 6.11 (m, 1H), 5.81 (m, 1H), 4.23 (s, 2H), 4.04 (s, 2H), 1.90 (s, 2H), 1.55 (s, 2H).

Synthesis of P7AC-*b*-PNIPAM-*b*-PSN_3

P7AC-*b*-PNIPAM-*b*-PSN_3block copolymers were synthesized by RAFT polymerization at 70°C using dithioester RAFT agent and azobisisobutyronitrile (AIBN) as reported in previous studies.[2-4] (Figure S1) Constituents consisting of 4-vinylbenzylchloride monomer, dithioester RAFT agent, and AIBN (mol of RAFT agent : mol of AIBN = 10:1)were added into a glass ampoule for polymerization under vacuum. Then, poly(4-benzylchloride) (PSCl) was precipitated by cold methanol. PSCl, *N*-isopropylacrylamide monomer, and AIBN in dimethylformamide (DMF) were added into a glass ampoule for sequential polymerization under vacuum. After polymerization, the products were precipitated in cold ether, filtered, and dried. Then, 7AC monomer and AIBN were added to PNIPAM-*b*-PSCl polymers to produce the third block of P7AC. After 24 hrs of reaction, the products were precipitated in cold ether and filtered. To avoid the coupling during the azidation of the PSCl group, the dithioester end group was converted to a thiol group by reaction with hexylamine. The solution was precipitated into cold ether. Then, P7AC-*b*-PNIPAM-*b*-PSCl was dissolved with sodium azide in DMF, and stirred at room temperature for 24 hr. The solution was filtered, and precipitated in cold ether, obtaining the white powder of P7AC-*b*-PNIPAM-*b*-PSN_3. The total M_n and PDI of the synthesized polymers were determined by SEC, which was calibrated by PS standards.

Preparation of fluorescent, thermally-responsive, polymer-anchored GO composites (FGO)

Graphene oxide (GO) was prepared *via* a modified Hummers method. Briefly, 1 g of graphite flakes was added to the mixture of 23 mL of H_2SO_4, 0.5 g of $K_2S_2O_8$, and 0.5 g of P_2O_5. After allowing the reaction to proceed under ambient conditions for 6 hr, the suspension was then filtered and dried. The dried graphite was added to 23 mL of H_2SO_4 solution in an ice bath. Then, 3 g of $KMnO_4$ was gradually added to the graphite solution for about 10 min. In the following 2 hr of stirring at 35^{o}C, 46 mL of DI water was added, and 15 min thereafter, 2 mL of H_2O_2 was added. The mixture was centrifuged and washed with 10% HCl aqueous solution. The washing process was repeated several times. The purified graphite oxide was suspended in DI water and exfoliated into individual GO sheets using a sonicator. To prepare FGO, GO (20 mg), P7AC-*b*-PNIPAM-*b*-PS$N_3$1 (200 mg, 0.013 mmol) and DMF (20 mL) were placed in a flask. A flow of argon was bubbled before the reaction for 1 hr. Then, the mixture was stirred at 160^{o}C for two days under an argon atmosphere. After being cooled to room temperature, the mixture was dissolved in DMF and filtered through a 220 nm PTFE membrane several times.

Characterization

Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AMX 500. The molecular weights (M_n) and polydispersity indices (PDI) of the synthesized polymers were obtained by size exclusion chromatography (SEC) using a Waters 1515 pump and a Waters 2414 differential refractometer with THF as the eluent at a flow rate of 1 mL/min. SEC was calibrated using PS standards. ATR-FTIR spectra were taken using a Bruker ALPHA. Thermo gravimetric analysis (TGA) was performed on a TA Q500 at a scan rate of 10^{o}C/min from room temperature to 600^{o}C under a N_2 atmosphere. The PL spectra were obtained using a Horiba Jobin Yvon NanoLog spectrophotometer with 325 nm as the excitation wavelength and a 10 mm quartz cuvette. The samples for PL measurements were prepared by dissolving FGO in a water at very low concentrations (1.0 mg/mL).

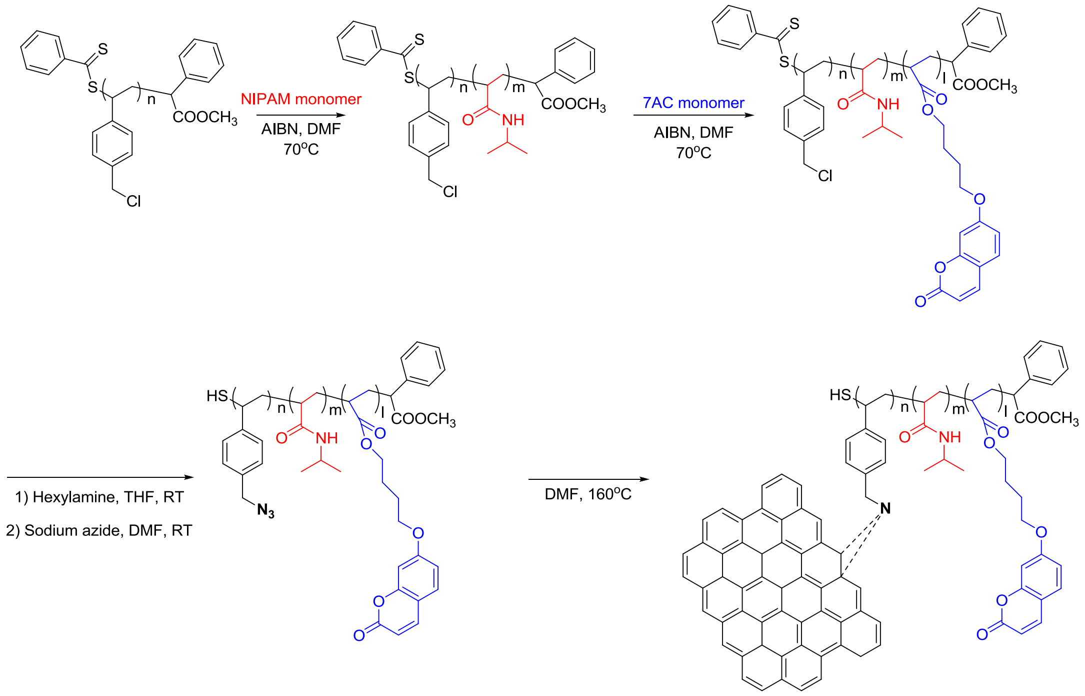

Figure S1. Synthesis of P7AC-*b*-PNIPAM-*b*-PSN$_3$ triblock copolymers and their use for preparation of FGO nanocomposites.

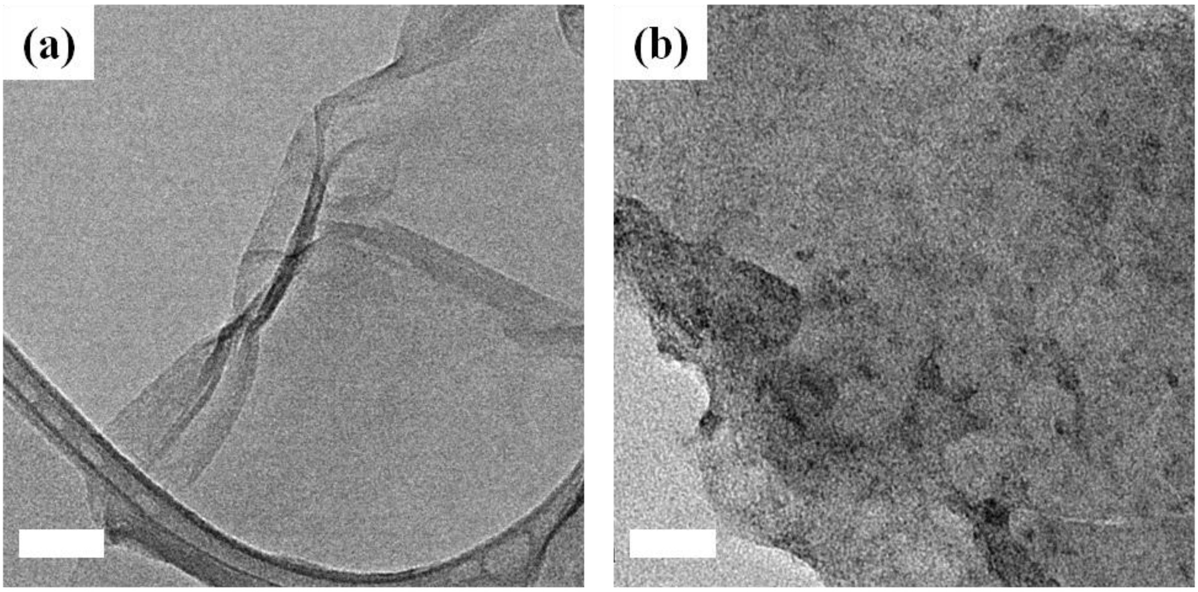

Figure S2. TEM Images of (a) GO and (b) FGO. The scale bar is 50 nm.

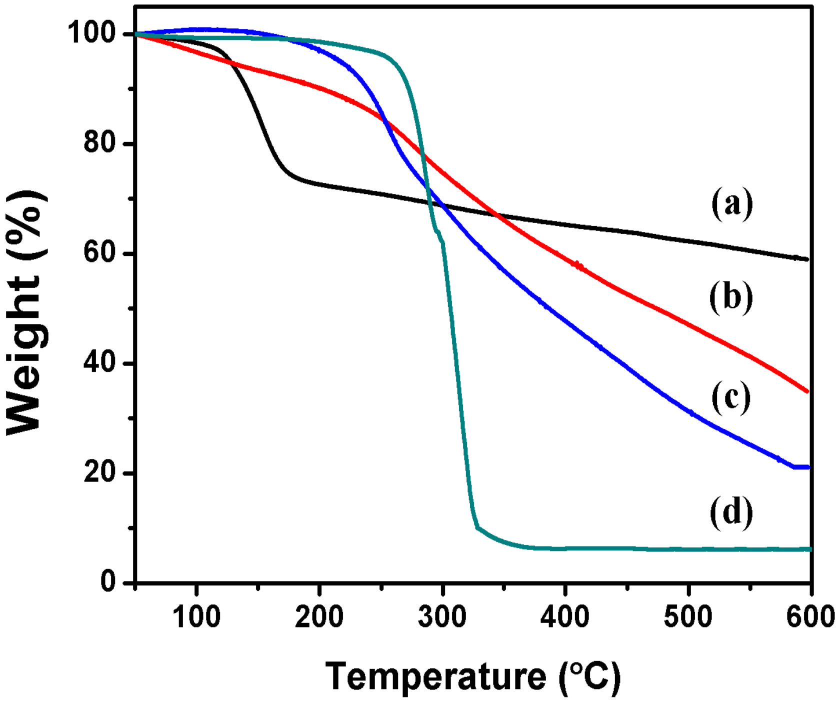

Figure S3. TGA curves of (a) GO, (b) FGO1, (c) FGO2 and (d) pristine P7AC-*b*-PNIPAM-*b*-PSN_3.

Figure S4. Photographic images of FGO2 in water under light (left) and UV Lamp at 365 nm (right).

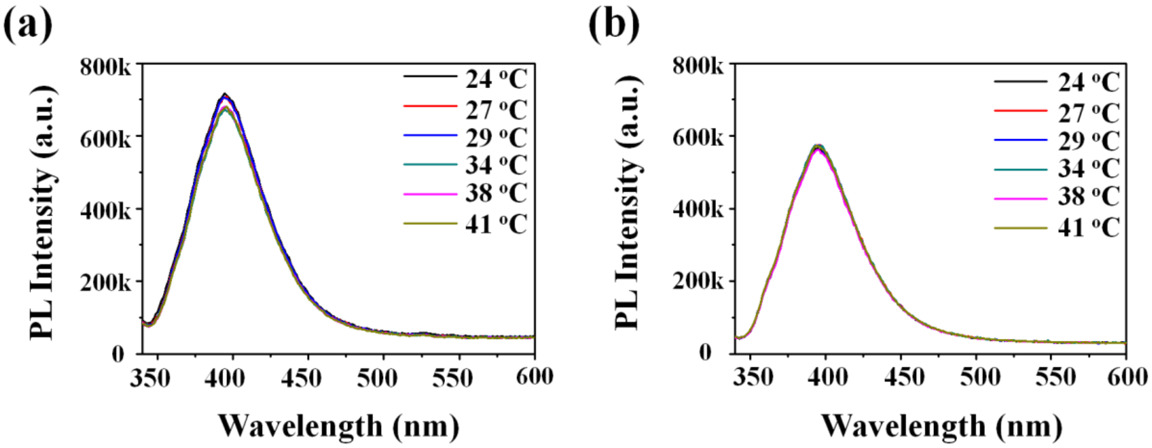

Figure S5. Photoluminescence spectra of (a) P7AC-*b*-PNIPAM-*b*-$PSN_3$1 and (b) P7AC-*b*-PNIPAM-*b*-$PSN_3$2 as a function of temperature.

References

(1) Feng, P.; Zhu, J.; Cheng, Z. P.; Zhang, Z. B.; Zhu, X. L. *Polymer*2007, **48**, 5859.
(2) M. Yoo, S. Kim, J. Lim, E. J. Kramer, C. J. Hawker, B. J. Kim and J. Bang, *Macromolecules*, 2010, **43**, 3570-3575.
(3) T. Kwon, T. Kim, F. b. Ali, D. J. Kang, M. Yoo, J. Bang, W. Lee and B. J. Kim, *Macromolecules*, 2011, **44**, 9852-9862.
(4) J. Lim, H. Yang, K. Paek, C.-H. Cho, S. Kim, J. Bang and B. J. Kim, *J. Polym. Sci. Pol. Chem.*, 2011, **49**, 3464-3474.
(5) Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.*1958, **80**, 1339.